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CATALYSIS IN THE DECOMPOSITION OF POTASSIUM CHLORATE

BY

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THESIS

FOR THE

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ENTITLED Catalysis in the Decomposition of Potassium Chlorate

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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I

INTRODUCTION

The decomposition of potassium chlorate is facilitated by certain substances which act as catalysts in the reaction. The catalytic effect includes a considerable lowering of the temperature at which the decomposition begins, and a tremendous increase in the rate at which the oxygen is given off. When potassium chlorate is heated alone, oxygen begins to come off at about 340°-350°, and manganese dioxide, heated alone, gives off oxygen, beginning at about 400° (Alex Smith), but with a mixture of the two, the evolution commences at about 225°, more than 100° lower. The rate of evolution of the gas increases very slowly as the temperature is raised until, at 305°, it suddenly becomes rapid, and at about 335° as the chlorate begins to melt, it is too great to be measured.

II

HISTORICAL

It is not known who was the first chemist to observe that certain catalytic agents accelerate the decomposition of potassium chlorate to give oxygen, but several men have added something to the knowledge of the subject in the last seventy-five years. The first contribution was that of Wachter, in 1843. Other prominent contributors were Baudrimont and Jungfleisch in 1871; Schulze in 1880; Hodgkinson, Lowndes, and Veley in 1888-89; Fowler and Grant in 1890; McLeod in 1889, 1894 and 1896; Brunck in 1893; and Sodeau in 1900; 1901, and 1902. (The most important results of these investigators is outlined below.) Nothing much of importance has been done on it since the work of Sodeau.

III

THEORETICAL

The Course of the Reaction.

A great many different reactions have been suggested for the decomposition and there still exists a great deal of disagreement on this question.

McLeod in 1896 considered the decomposition to be a chemical reaction, which involved the catalyst (approximate reactions):

$$2\ KClO_3 + 2\ MnO_2 = 2\ KMnO_4 + Cl_2 + O_2$$

$$2\ KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

$$K_2MnO_4 + Cl_2 = 2\ KCl + MnO_2 + O_2$$

He found, also, that the particles of MnO_2 are broken up during the decomposition by examining them with a microscope. Baudrimont and Veley claim than an evolution of oxygen can be produced without fusing the chlorate and with no catalyst present. And since many inert substances, such as SiO_2 do not have a catalytic effect, Sodeau stated that what actually took place was probably a chemical reaction involving the catalyst, rather than a physical effect due to contact.

Sodeau also reasoned that the chlorate probably undergoes self-oxidation when heated alone, and the perchlorate

is formed:

$$4\ KClO_3 + 61{,}300\ cal. = KCl + 3\ KClO_4$$

His idea is confirmed by the following facts:

$$4\ KClO_3 \xrightarrow{-\ 39{,}000\ cal.} 4\ KCl + 6\ O_2$$

$$4\ KClO_3 \xrightarrow{+\ 61{,}300\ cal.} 3\ KClO_4 + KCl$$

Then by Hess's law:

$$3\ KClO_4 + KCl \xrightarrow{-\ 100{,}300\ cal.} 4\ KCl + 6\ O_2$$

Since any reaction (favored by high Temperature) will always take place in the direction in which heat is absorbed, the above reaction will go through the formation and decomposition of the perchlorate at the expense of the other one. Consequently unless a catalyst is present, the perchlorate is always formed as an intermediate compound. This reaction occurs only at a temperature of 340° or higher. At this temperature, only a small amount of the total oxygen present in the chlorate is given off, as shown by Remsen's equation, and confirmed by experimental results:

$$8\ KClO_3 = 5\ KClO_4 + 3\ KCl + 2\ O_2$$

But when a catalyst is present, no perchlorate is formed, even temporarily from the chlorate, according to Sodeau, since

Eccles found none in the residue on analysis, and McLeod showed that if it was once formed, it would not be decomposed under the conditions of the experiment, so that the reaction is probably

$$2\ KClO_3 = 2\ KCl + 3\ O_2 \quad \text{(Mellor)}$$

or one similar to it.

IV

EXPERIMENTAL

a. Materials.

C. P. $KClO_3$ was used in all of the determinations. The crystals were very fine and white. The commercial MnO_2 used was found on analysis to contain 91.07% MnO_2, and 8.82% Fe_2O_3. The pure MnO_2 was prepared after the method of Georgen. C. P. Manganese carbonate was added in excess to nitric acid. The crystals of $Mn(NO_3)_2$ were washed and changed to MnO_2 by heating at 300°. The other catalysts employed were the impure compounds:

A charge was prepared as follows: The $KClO_3$ and catalyst in weighed proportions, were mixed thoroughly, ground in a porcelain mortar, moistened with distilled water and dried. In this way, the catalyst was deposited on the surface, and in the pores of the $KClO_3$ in a finely divided form, and in intimate contact with it. A charge consisted of 6 g. of $KClO_3$, plus an amount of the catalyst calculated as a certain percentage of the total weight. For example, in the table, $KClO_3$ plus 25% of MnO_2, refers to 6 g. of the chlorate mixed with 2 g. of the dioxide.

b. Apparatus.

The apparatus used to study the decomposition was essentially as shown in Fig. 1. The reaction tube was a Pyrex glass test-tube 2.5 by 20.5 cm. The charge occupied a length of from 2 to 3 cm. in the bottom of the tube. The flask was also of Pyrex glass 5 by 25 cm. The gas was collected by downward displacement of water in a 100 cc. eudiometer. The furnace was connected to 110 A.C. terminals, the current being cut down to a suitable amount by means of a carbon resistance. The temperature was measured with a 360° thermometer, with the bulb placed in the reacting mixture. The temperature of the charge was kept constant by means of a constant boiling liquid in the bottom of the flask. Benzoic acid was used for a temperature of 235°, acetanilid for 300°, and anthracene for 328°. The variation in temperature was within 2°.

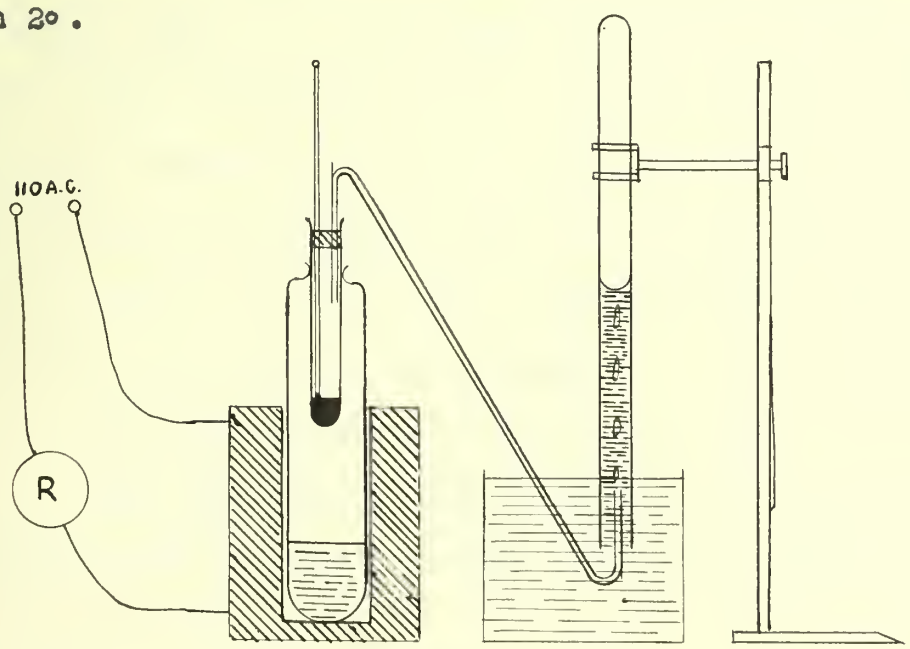

Fig. 1

V

EXPERIMENTAL RESULTS.

a. Qualitative tests.

The temperatures chosen were 235°, 300°, and 328°. Below 235°, the decomposition was too slight to be appreciable, and above 328°, too violent to be controlled or measured. The boiling points and suitability of the liquids also had to be considered.

As a basis for comparison, a charge was run without any catalyst present. This was followed by experiments on silica, sodium chloride, sodium sulfate, sodium carbonate, alumina, cobalt sulfate, zinc oxide, molybdenum oxide, stannic oxide, barium dioxide, bismuth oxide, and mercuric oxide, none of which exerted a catalytic influence on the reaction.

Cr_2O_3, Co_2O_3, and Ni_2O_3 each caused the chlorate to give off both oxygen and chlorine at a tremendous rate, even below 235°, due to the fact that they reacted with the chlorate, liberating part of the oxygen and all of the chlorine. The probable reaction for the Cr_2O_3 is given below. $K_2Cr_2O_7$ was tested for, and found in the residue.

$$Cr_2O_3 + 2\ KClO_3 = K_2Cr_2O_3 + Cl_2 + O_2$$

CuO, MgO, Pr_4O_7, Nd_2O_3, MnO_2, and Fe_2O_3 all facilitated the reaction, but the last two, only, showed a consider-

able catalytic effect, and were the only ones that were studied in detail. The results are shown in the accompanying table. The data on MnO_2 and Fe_2O_3 is represented graphically in Figures 2,3,4,5,6,7 and 8. The effect of varying the temperature, and the amount of catalyst is clearly indicated in these curves. The rate of the evolution of oxygen was measured in cubic centimeters per minute at 22°, and 760 mm. pressure.

b. Nature of the catalyst.

Sodeau showed that any reaction other than one including alternate oxidation, and deoxidation of the catalyst would involve setting free of all of the chlorine, and its subsequent complete reabsorption, and since the amount of chlorine given off is very small, the catalyst is the oxygen carrier. An intermediate compound is probably formed between the catalyst and the oxygen which is a surface complex of indefinite and variable composition. This substance is unstable and is almost immediately broken up again into the catalytic agent and oxygen. The only substances which could act as catalysers, would be then, oxides of metals, capable of more than one valence. This was actually found to be the case, since the oxides of copper, magnesium, praseodymium, neodymium, manganese, and iron were

the only catalysers, and all of these are oxides of metals with at least two valences. There seems to be some doubt as to the existence of another oxide of magnesium besides MgO, but Roscoe and Schorlemmer state that MgO_2 exists, but is unstable. Magnesium would not, then, be an exception. However, there are metals which, it would seem, ought to catalyse the reaction, such as barium and calcium, both of which form two oxides. For some unknown reason such metals are exceptions to the rule.

c. Relative Activity of Catalysts.

The table shows that MnO_2 and Fe_2O_3 are the only efficient catalysts for the reaction, and that MnO_2 is almost twice as active as Fe_2O_3 in increasing the rate of gas evolution. Prasedymium oxide is next most active, then the oxides of copper, magnesium, and neodymium in the order mentioned. Manganese dioxide seemed to have the greatest effect in lowering the temperature of decomposition. With MnO_2, the oxygen began to come off at about 225°, with Fe_2O_3, the evolution began at a trifle higher temperature, and so on for the others. So the temperature at which the decomposition begins is inversely proportional to the activity of the catalyst in question, in increasing the rate of gas evolution.

d. Effect of Varying Percent of Catalyst.

The effect of varying the amount of catalyst is shown clearly in Figures 4, 5, 6 and 7 for the three temperatures 235°, 300°, 328°. The optimum concentration for both MnO_2 and Fe_2O_3 was about 33%. Experiment showed also that the optimum concentration did not vary with the temperature, and that the amount of catalyst present had no effect in lowering the temperature of decomposition.

e. Promoter Action.

Impure MnO_2 was found to be more active than the pure MnO_2. Analysis showed this to be due to the presence of some Fe_2O_3 as an impurity. So a charge was made up of 22.8% pure MnO_2 and 2.2% pure Fe_2O_3, the proportions existing in the impure MnO_2. As shown in the table, this mixture gave essentially the same results as did the impure MnO_2. This is evidence for the belief that the Fe_2O_3 exerts a promoter action on the MnO_2 in catalysing the reaction and vice versa. This action was studied with various concentrations of both catalysts at the three different temperatures. The results are shown graphically in Figure 8. The optimum concentration was found to be 50% of each catalyst. This mixture was much more active than 100% of either one.

VI

SUMMARY

1. A number of substances have been tested for a catalytic effect upon the decomposition of potassium chlorate. Only certain metallic oxides are active in this respect.

2. The two best accelerating agents, MnO_2 and Fe_2O_3 have been studied at several temperatures, and in varying concentrations. The optimum concentration of the catalyst has been found to be approximately 33% by weight.

3. Promoter action is indicated by the fact that the activity of MnO_2 is improved by an admixture of Fe_2O_3, and vice versa. The superior activity of pyrolusite to pure MnO_2 is thus explained by the presence of Fe_2O_3 as an impurity in the ore.

4. A sudden, abnormal increase in the rate of the evolution of oxygen at about 305° (as illustrated in the curves) indicates that this is a critical point in the decomposition.

5. It appears from available data that the effect of heating $KClO_3$ alone may be expressed by two concurrent reactions:

(1) $4\ KClO_3 = 3\ KClO_4 + KCl$

(2) $2\ KClO_3 = KCl + 3\ O_2$

of which the first is of much greater magnitude, especially if the temperature is low. The $KClO_4$ subsequently decomposes at a higher temperature into KCl and oxygen.

6. In the presence of a catalytic agent, the decomposition of $KClO_3$ proceeds by the second equation, at the expense of the first, or more probably, by an entirely different route, in which an intermediate compound is formed between oxygen and the catalyst. This compound is unstable and is probably of indefinite and variable composition - of the nature of a surface complex. This conclusion would seem to be supported by the fact that the only substances which are active accelerating agents are the oxides of metals capable of more than one valence.

Material % Catalyst	CC. O_2 per minute 235°	300°	328°
$KClO_3$ (6 g.)	----	0.35	1.0
7.7 MnO_2	1.9	3.55	32.5
14.3 MnO_2	3.55	5.0	59.0
25.0 MnO_2	5.95	8.0	94.5
29.4 MnO_2	7.8	8.6	112.0
33.3 MnO_2	8.3	12.4	119.5
40.0 MnO_2	8.1	12.0	115.5
50.0 MnO_2	7.5	11.5	104.2
14.3 Fe_2O_3	2.1	3.3	34.0
25.0 Fe_2O_3	3.6	5.3	51.5
33.3 Fe_2O_3	4.85	6.65	62.0
40.0 Fe_2O_3	4.3	6.4	59.0
50.0 Fe_2O_3	3.5	5.85	51.0
18.75 MnO_2 } 6.25 Fe_2O_3 }	7.0	11.2	99.1
18.75 Fe_2O_3 } 6.25 MnO_2 }	6.0	9.5	89.0
12.5 MnO_2 } 12.5 Fe_2O_3 }	7.9	12.25	116.5
25.0 CuO	0.95	1.95	24.0
25.0 Pr_4O_7	2.25	3.75	28.0
25.0 Nd_2O_3	0.45	0.65	5.05
25.0 MgO	.45	.8	7.25
25.0 MnO_2(C.P.)	1.8	2.6	27.5
22.8 MnO_2(C.P.) 2.2 Fe_2O_3	5.7	7.8	86.0

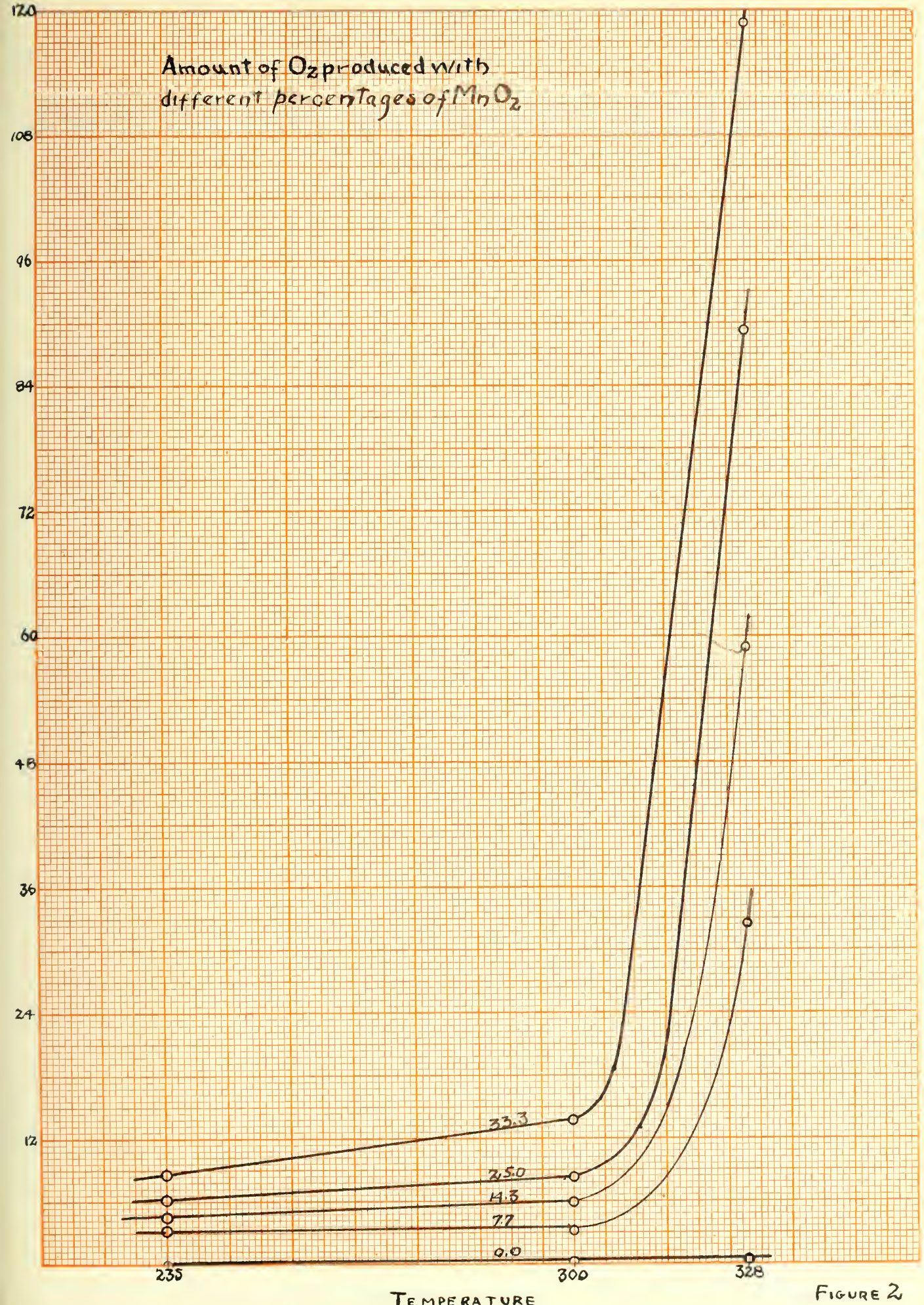
Amount of O_2 produced with different percentages of MnO_2
120
108
96
84
72
60
48
36
24
12
33.3
25.0
14.3
7.7
0.0
235
300
328
TEMPERATURE

FIGURE 2

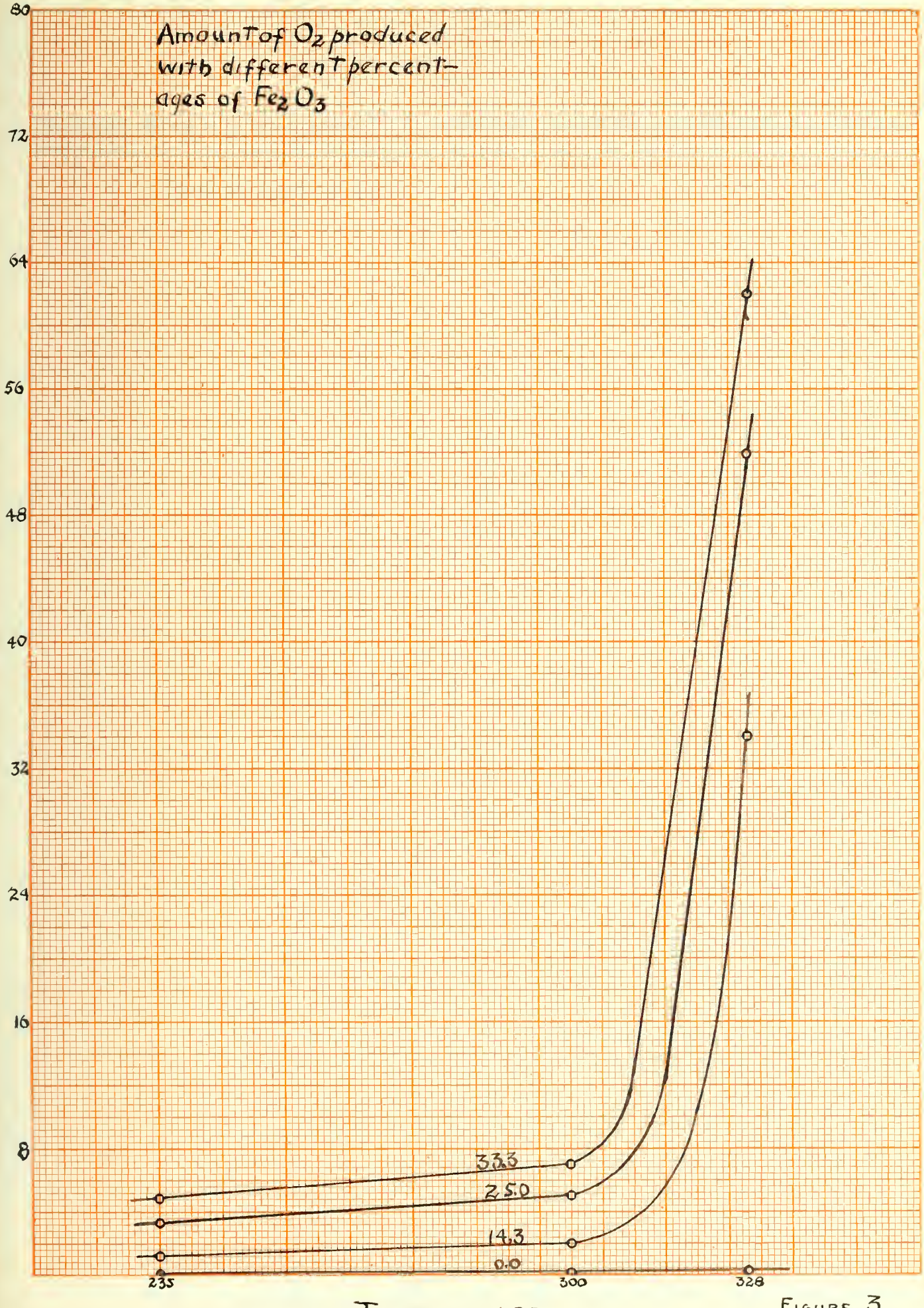
Amount of O_2 produced with different percentages of Fe_2O_3
80
72
64
56
48
40
32
24
16
8
33.3
25.0
14.3
0.0
235
300
328
TEMPERATURE

FIGURE 3

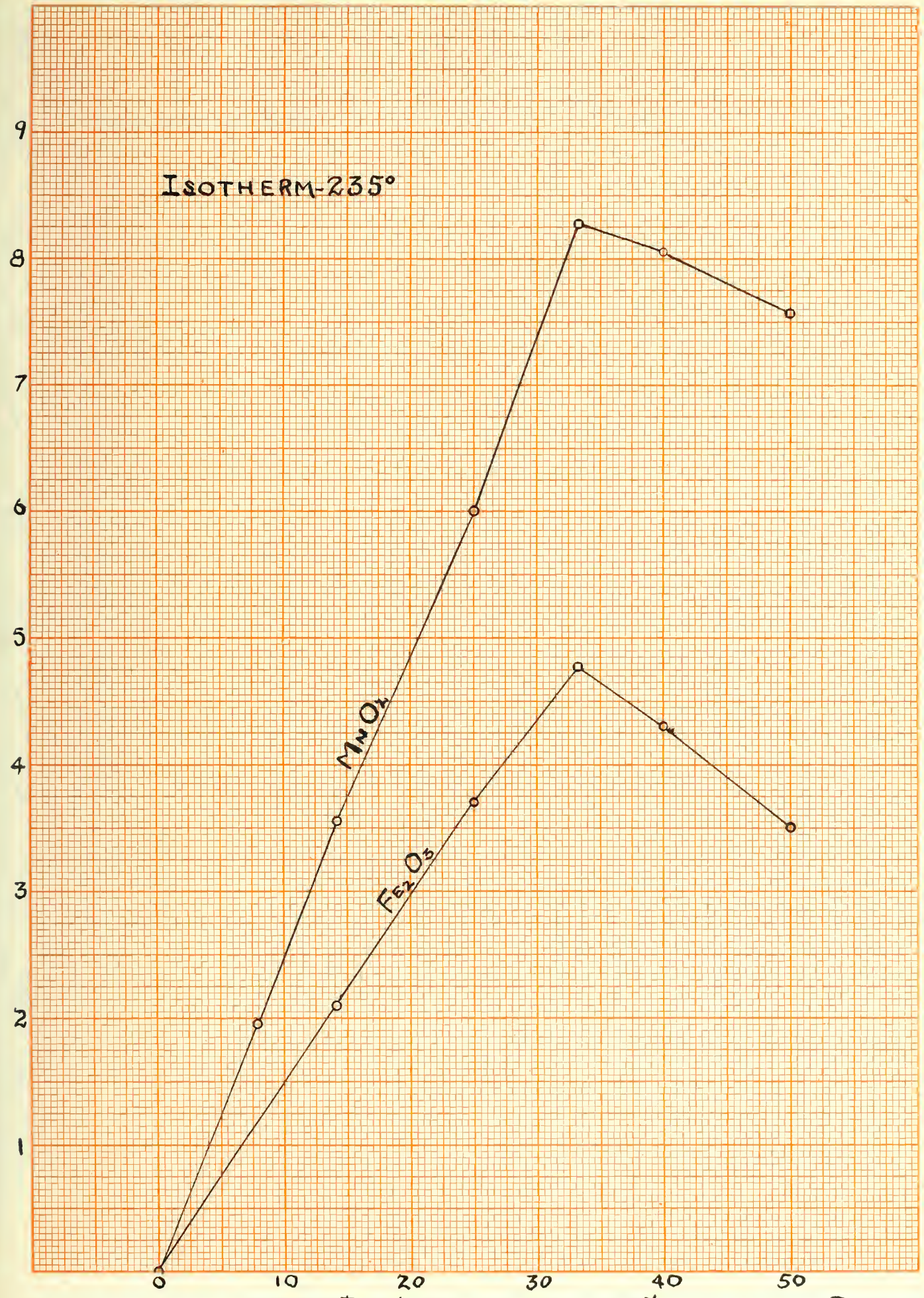
ISOTHERM-235°
MnO2
Fe2O3
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
concentration in percent

FIGURE 4

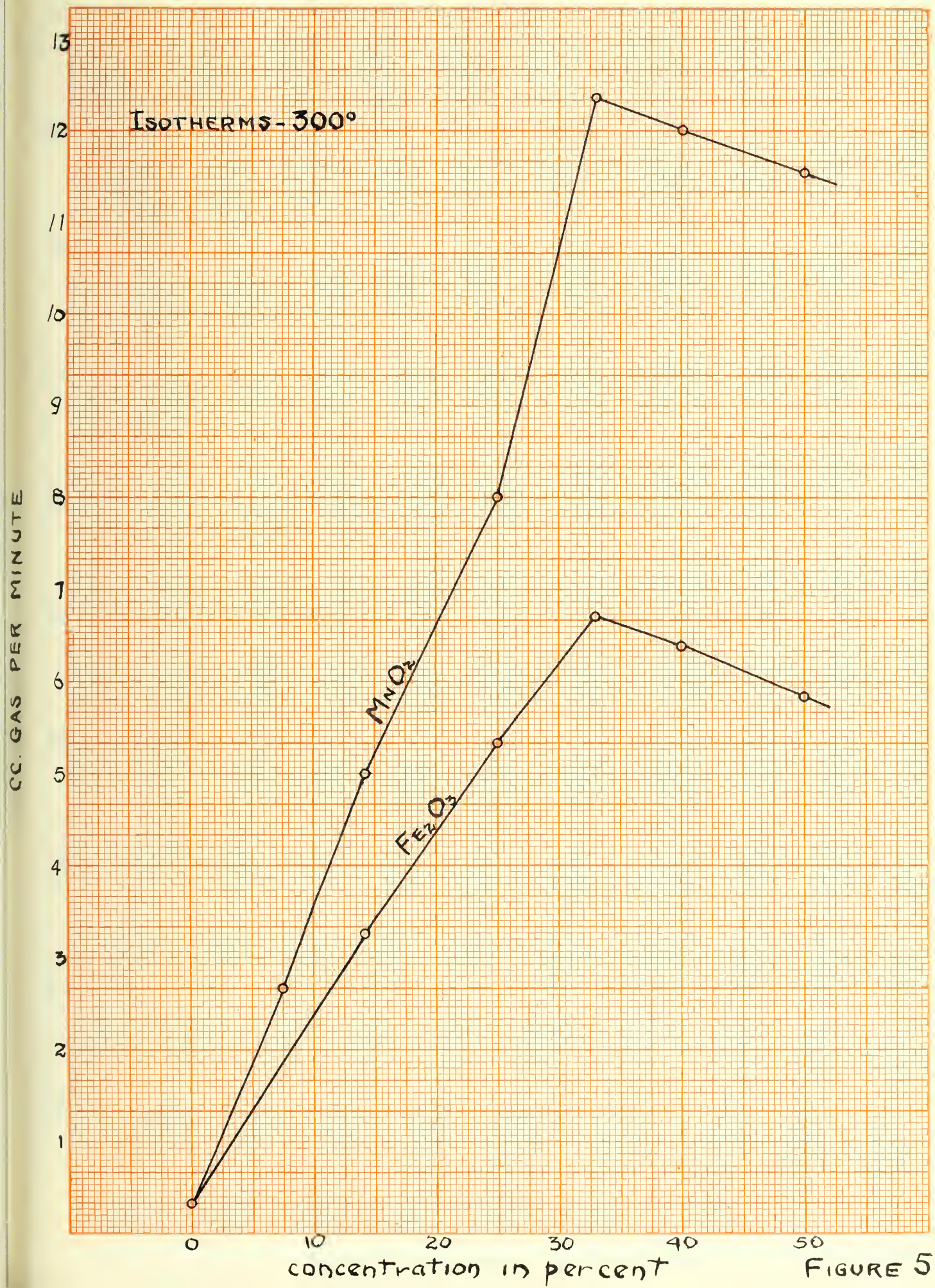
ISOTHERMS - 300°
MnO2
Fe2O3
CC. GAS PER MINUTE
13
12
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
concentration in percent

FIGURE 5

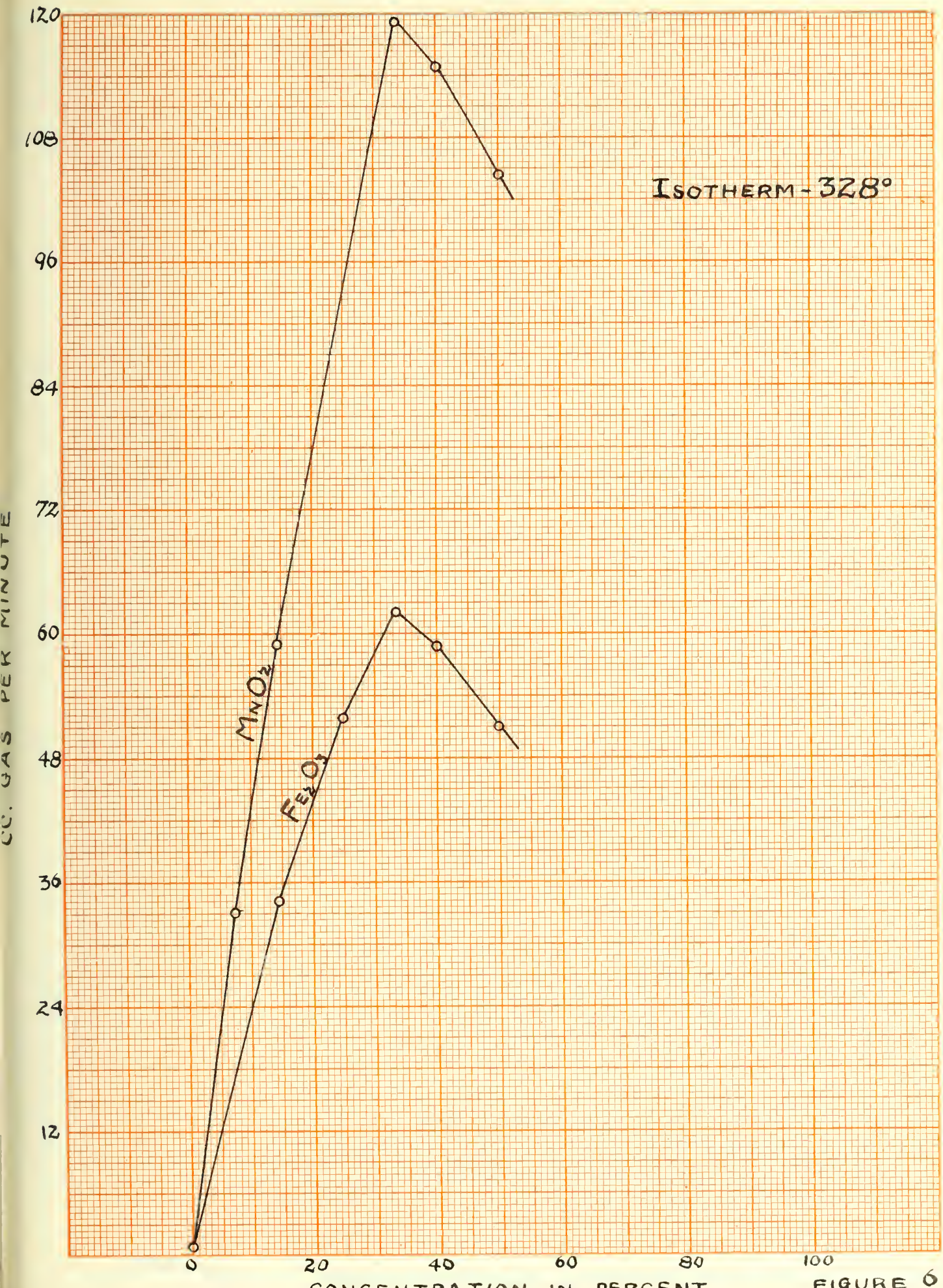
120
108
96
84
72
60
48
36
24
12
CC. GAS PER MINUTE
ISOTHERM - 328°
MnO2
Fe2O3
0
20
40
60
80
100
CONCENTRATION IN PERCENT

FIGURE 6

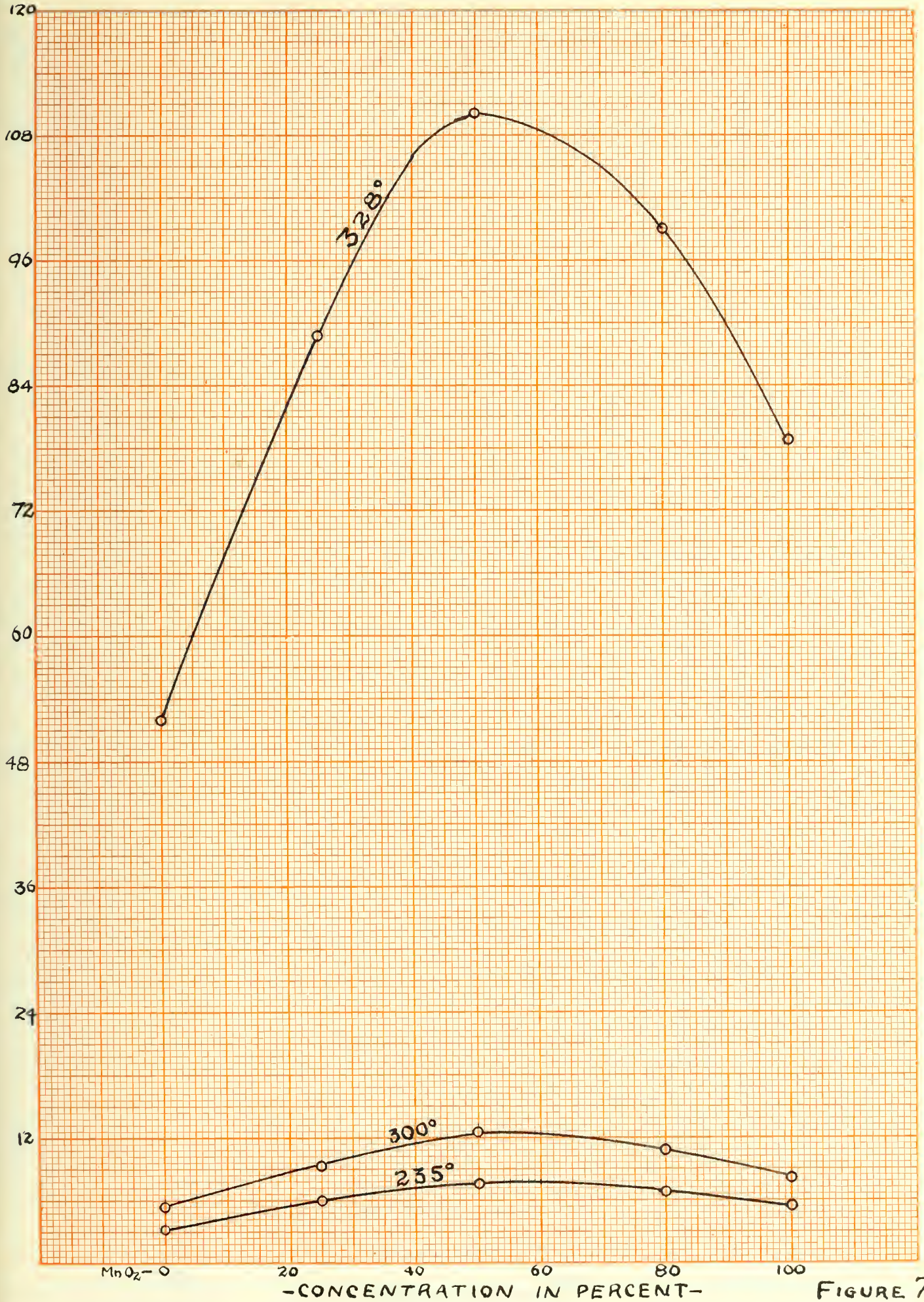
120
108
96
84
72
60
48
36
24
12
CC. GAS PER MINUTE
328°
300°
235°
MnO2- 0
20
40
60
80
100
-CONCENTRATION IN PERCENT-
Fe2O3-100
80
60
40
20
0

FIGURE 7

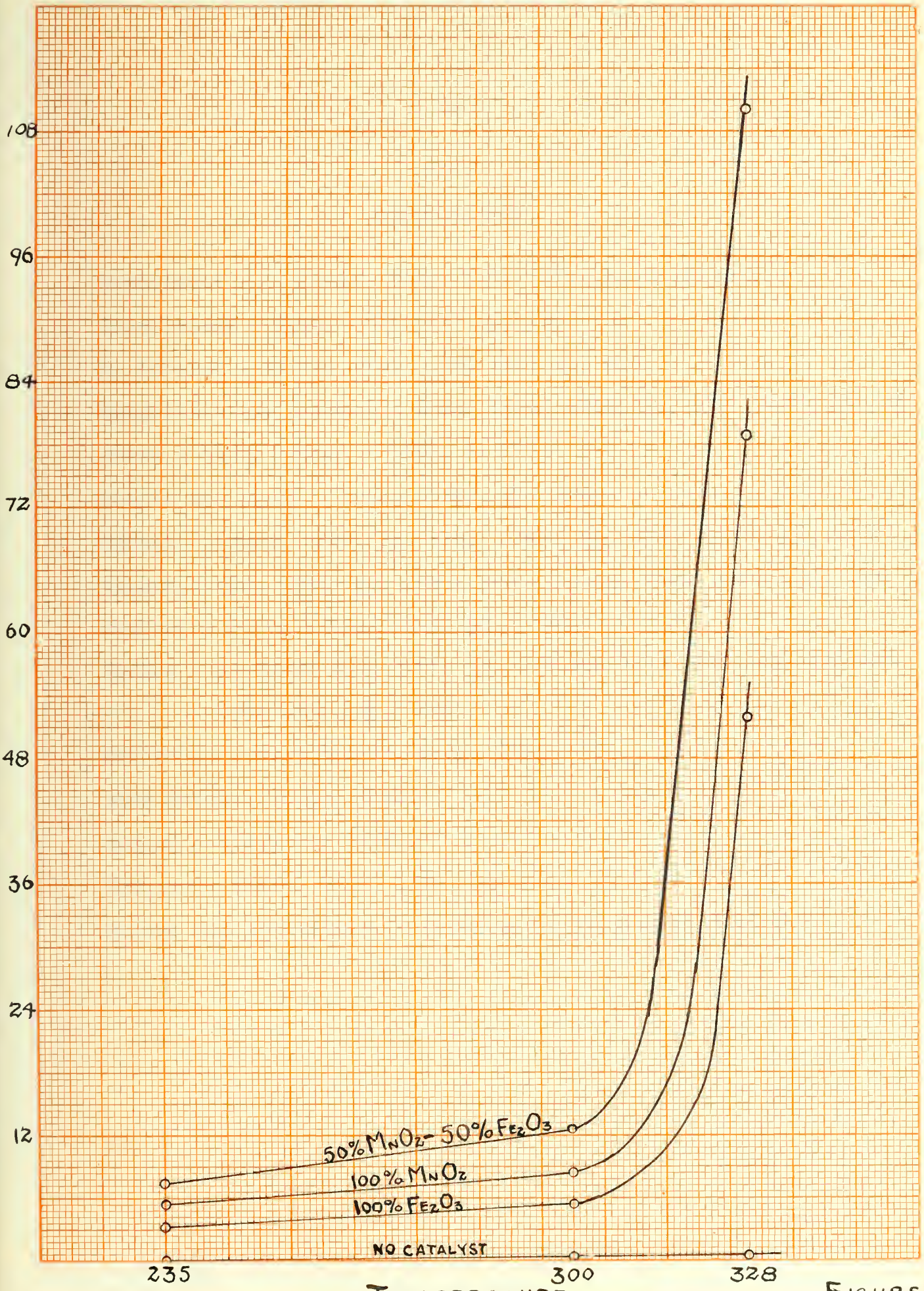
108
96
84
72
60
48
36
24
12
50% MnO2 - 50% Fe2O3
100% MnO2
100% Fe2O3
NO CATALYST
235
300
328
TEMPERATURE

FIGURE 8

VII.

BIBLIOGRAPHY

Baudrimont - J. Pharm. Chim. 1871 (IV) 14, 81 and 161.

Jungfleisch - ibid 1871 (IV) 14, 130.

H. Schulze - J. Pr. Chem. 1880 (II) 21, 426.

Hodgkinson and Lowndes - Chem. News, 1888, 58, 309; 1889, 59, 63

Veley - Phil. Trans. - 1888, A. 271.

Fowler and Grant - Trans. 1890, 57, 272.

McLeod - Trans. 1889, 55, 184; 1894, 64, 202: 1896, 69, 1015.

Brunck,- Ber. 1893, 26, 1790; Zeit. Anorg. Chem. 1895, 10, 222.

Wachter - J. Pr. Chem. 1843, 30, 325.

Sodeau - J. Chem. Soc. 1900, 77, 137 and 717; 1901, 79, 247 and 939; 1902, 81, 1066.

Mellor , J. W. - Modern Inorg. Chem.

Alex Smith - Inorg. Chem.

Remsen - Chemistry (1906)

Georgen - Compt. rend. 1879, 88, 797.

Roscoe and Schorlemmer - Treatise on Chemistry, Vol. 2.

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